Isotopic provenancing of Pb in Mitrovica, northern Kosovo: source identification of chronic Pb enrichment in soils, house dust and scalp hair.

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ABSTRACT

Mitrovica, northern Kosovo, is the site of some of the highest Pb concentrations reported in human populations; exemplified by Pb concentrations in scalp hair of up to 130 μg g^{-1} and widely-publicized of Pb-related ill-health and mortality amongst internally displaced populations. High human Pb burdens are accompanied by elevated concentrations of potentially harmful elements (PHEs) in soils and house dust within the city, which has a long history of mining and metallurgy. In this study enrichment-levels for PHEs in soils are quantified and compared to environmental quality guidelines and a statistically-derived estimation of background concentration. In addition, Pb isotopes ($^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$) are used to characterise the isotopic signatures of potential point sources of Pb and a mixing model employed to quantify the contribution of sources to Pb present in soils, house dust, and the scalp hair of children and young people. Pb isotopic evidence suggests that Pb in surface soils and house-dust is predominantly sourced from historical deposition of Pb-containing aerosols from metal smelting, with lower contributions from wind-blown dispersal of metalliferous waste. Pb present in scalp hair is interpreted as the result of non-occupational exposure and the ingestion and/or inhalation of Pb-enriched surface soil and house dust. This study represents one of the very few instances where this type of geochemical tracing technique has been successfully applied to definitively identify the source of Pb present within biological samples. The results of this study are of particular relevance to environmental management and highlight the human health risk posed by the legacy of now inactive mining and metallurgy in addition to the challenge posed in mitigating the risk posed by diffuse soil pollution.

KEYWORDS: lead isotopes, mixing model, metals, soil, scalp hair

HIGHLIGHTS:

- Enrichment of soils, house dust and scalp hair with potentially harmful elements
- Lead isotopes used as geochemical fingerprints to characterize PHE sources
- Mixing model quantifies the Pb inputs from anthropogenic and geogenic sources
- Legacy of smelting activity in environmental pollution
- Role of soils and house dust as a Pb source of Pb to humans

1. INTRODUCTION

The mining, smelting and processing of metal ores are widely recognised as major sources of potential harmful elements (PHEs) within the environment (Allan, 1997; Bacon and Dinev, 2005). The consequent dispersal of these PHEs through fluvial (Bird et al., 2008; Turner et al., 2008) and atmospheric (Sonke et al., 2008) processes often results in widespread enrichment of soils (Dennis et al., 2009; Jung and Thornton, 1996), river water and river channel sediment (Bird et al., 2010a; El Khalil et al., 2008; Hutchinson and Rothwell, 2008), floodplain sediments (Hurkamp et al., 2009; Lewin and Macklin, 1987), vegetation (Barman et al., 1999; Fytianos et al., 2001; Zaman and Zereen, 1998) and fauna (Nannoni et al., 2011). The impact of anthropogenic activity on modern-day PHE accumulation in the environment is significant, with an estimated 95% of total Pb deposition (Alfonso et al., 2001; Geraldes et al., 2006), and an estimated 96-99% of atmospheric Pb fallout (Erel et al., 1997) derived from anthropogenic sources.

The deleterious effects of PHEs, especially Pb, on human health are widely recognised and have been related to exposure from drinking water (Bird et al., 2009), edible vegetation (Komárek et al., 2007), house dust (Bosso and Enzweiler, 2008; Spalinger et al., 2007) and atmospheric particulates (Okorie et al., 2012). Children have been identified as being particularly susceptible to PHE uptake through behavioural characteristics such as hand-to-mouth action (Hwang et al., 1997; Loiacono et al., 1992). This uptake route is particularly significant in areas where families either live on, or adjacent to, land contaminated with PHEs, or where metal smelting and reprocessing activities take place in close proximity to housing (Boisa et al., 2013; Pelfrene et al., 2012).

In the last decade lead isotopes have been increasingly used as geochemical tracers in environmental studies (Bird, 2011; Komárek et al., 2008), and they have been shown to be a very powerful tool for discriminating between multiple contaminant sources (e.g. Baron et al., 2009; Bird et al., 2010b; Ettler et al., 2006; Ip et al., 2007). Lead within the environment is present as four main isotopes: ^{204}Pb, which is a stable, and the long-lived radiogenic isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb, that are the daughter products of the decay of ^{238}U, ^{235}U and 2^{32}Th, respectively (Houtermann, 1946). The relative abundance of each of the four Pb isotopes within bedrock and Pb ores will vary according to the primordial concentrations of ^{238}U, ^{235}U and ^{232}Th, and the length of the decay processes (Doe, 1970). Of particular relevance to tracing metal dispersal pathways and fingerprinting contaminant sources, is the fact that naturally- and anthropogenically-sourced Pb often have different and distinguishable isotopic compositions (Bacon, 2002).

In Mitrovica, northern Kosovo, the release of PHEs from poorly-regulated mining and smelting industries has resulted in the severe enrichment of Pb and other PHEs within surface soils and river water (Behrami et al., 2008; Borgna et al., 2009; Stafilov et al., 2010). Furthermore, Pb mining and metallurgy in the Mitrovica region, as well as poorly managed storage of mine, smelter and industrial waste (Peck, 2004), is believed to have resulted in the most significant modern case of human Pb poisoning in Europe. High Pb levels in blood (Wasserman et al., 2000; Wasserman et al., 1997) and hair (Runow, 2005b) have been linked to instances of Pb-related intellectual impairment and mortality in displaced refugee populations (Factor-Litvak et al., 1999; Lamb et al., 2008). Whilst soils in the Mitrovica urban area have been investigated for their PHE content (Borgna et al., 2009) and the bioaccessibility of PHEs (Boisa et al., 2013), there has been no attempt to date to definitively identify the source of Pb present in environmental and biological media and to assess how Pb source relates to possible human exposure routes.

In the light of this critical data gap, the aims of this study are twofold: first, to quantify PHE levels (principally Pb) in Mitrovica from samples of (i) mine and metallurgical waste, (ii) soils and (iii) house dust. Second, to provenance the source of Pb within environmental and biological (scalp hair) samples using Pb isotope signatures as a geochemical tracer. Whilst Pb isotopes have been utilized to trace Pb dispersal in riverine sediments (Ettler et al., 2006; Miller et al., 2002) and soil (e.g. Mihaljevič et al., 2006), few attempts have been made to provenance Pb in samples of human hair (e.g. Gulson, 2008).

2. STUDY AREA

Mitrovica is located on the confluence of the Rivers Ibar and Sitnica in northern Kosovo. There has been metal mining and smelting within the region for over 2000 years, however, in 1926 the Trepča mining enterprise was founded to exploit the exclusive rights to mineral exploration at Stan Tërg to the northeast of Mitrovica (Palairet, 2003) (Figure 1). Stan Tërg comprises a Miocene-age Pb-Zn-Ag skarn deposit in the form of a massive to submassive lens, with occasional sulphide veins, hosted within a Palaeozoic-age host geology (MonTec, 2007). Lead and Zn production peaked in the 1930s (62,784 t and 53,191 t, respectively) with ore grade quality ranging between 6% (Zn) and 8% (Pb) (Sostaric et al., 2011). Ore production fell sharply during the Second World War but then quickly recovered by the early 1950s. In the latter half of the twentieth century combined Pb and Zn ore production steadily declined and had fallen to 10,295 t by the start of the 1998 war in Kosovo.

Metal ores were processed (via floatation) at Tuneli Pare and smelted at Zvečan (Figure 1) along with ores from elsewhere within the region. Tailings produced from ore flotation were stored in the Zharkov Potok

tailings pond, whilst waste from the Zvečan smelter was stored in the Gornje Polje slag heap located adjacent to the River Ibar (Figure 1). In 1987 a new Zn electrolysis plant opened in the Trepča Industrial Complex in the southeast quarter of the city (Figure 1). Uncovered industrial waste generated from this now disused plant, and from an adjacent chemical/battery factory, covers an area of approximately 30 ha on the banks of the Sitnica River (Figure 1). In total, c. 30 M tonnes of waste from metallurgical industries is stored in and around the Mitrovica urban area.

During the 1999 conflict in the former Yugoslavia, an 8,000 strong Roma, Ashkali and Egyptian (RAE) community was displaced from the Roma Mahalla suburb of Mitrovica, northern Kosovo (Figure 1). A proportion of this internally displaced population (IDP) was housed in camps at Cesmin Lug, Kablare and Osterode in Mitrovica (Figure 1). These camps are situated between 2 km and 0.8 km downwind of the Zveçan lead smelting complex and the Gornje Polje waste dumps. Following concerns over impacts to human health posed by PHE levels, numerous health surveys have been conducted involving the analysis of blood (WHO, 2004), hair (Runow, 2005), plants (Riccobono et al., 2004; Borgna et al., 2009), water (Behrami et al., 2008) and sediment (Riccobono et al., 2004). Since 2012 the remaining RAE population has been rehoused to redevelopments in Roma Mahalla and Bosniak Mahalla (Figure 1).

3. METHODS

3.1. Sampling and analysis of samples

Soil, mining/industrial waste, house dust and human scalp hair samples were collected in December 2009 and 2011 from a variety of sites in Mitrovica (Figure 1). To characterize the geochemical signatures of potential contaminant sources, samples of mine tailings, smelter waste and industrial waste (n = 12) were collected from the Zharkov Potok, Gorne Polje and Trepča Industrial Complex waste dumps. To establish the magnitude and extent of contaminant dispersal from these sources, a total of 182 soil samples were collected Roma Mahalla, Bosniak Mahalla, the Cesmin Lug and Osterode IDP camps and from sites across the Mitrovica urban area. At each site up to three samples were collected with a stainless steel trowel and Edelman soil auger from 0-10 cm (surface soil), 10-30 cm (shallow sub-surface soil) and 30-50 cm (deep sub-surface soil). In addition, samples of house dust (n = 7) were collected using a nylon brush from occupied dwellings in the Cesmin Lug and Osterode camps and from unoccupied houses in Roma Mahalla. Finally, to assess the uptake of metals (principally Pb) by the RAE communities, 10 samples of scalp hair were sampled using stainless steel scissors from children and young people (aged 1-21 years) living in the Cesmin Lug and Osterode camps.

In the laboratory, soil and mining/industrial waste samples were air dried at room temperature, disaggregated using a pestle and mortar and sieved through a 2 mm nylon mesh. Sub samples of the disaggregated < 2 mm fraction were digested for 1 hour in concentrated HNO_3 at 100°C. Lead and Zn concentrations were determined using a Perkin Elmer Atomic Absorption Spectrophotometer (AAS) and Cd and Cu by a Thermo-Finnegan Element2 Magnetic Sector-ICP-MS (MS-ICP-MS). Samples of house dust were digested and analysed as above after being sieved to isolate the <63 µm fraction. Analytical precision of PHE analyses ranged from 1 to 7%, with analytical accuracy versus two reference materials (ABS1 [a mid-Wales soil]) and CANMET2 [a Canadian soil]) ranging from 3 to 10 % and 2.5 to 13 %, respectively.

Methods for the preparation and analysis of scalp hair samples have been reported elsewhere (Boisa et al., 2013). In short, washed hair samples were digested in 50% HNO_3 under reflux and Pb concentrations determined by Thermo-Finnegan Element2 MS-ICP-MS. Analytical precision of Pb determinations was 5.4%, whilst analytical accuracy, assessed against the NCSDC73347 reference material (Chinese human hair), was 12%; this relatively low analytical accuracy was due to low Pb concentrations (8.8 ±1.1 µg g^{-1}).

Lead isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) were determined in a selection of soil, house-dust, mining/industrial waste and hair samples using a Thermo-Finnigan Element2 MS-ICP-MS. Samples were analysed in triplicate in batches of 5 along with blank samples and the NIST981 reference material. Analytical precision was found to be 0.13 % for both $^{206/207}Pb$ and $^{208/206}Pb$. Analytical accuracy versus the NIST981 standard was 0.30 % ($^{206/207}Pb$) and 0.24 % ($^{208/206}Pb$). Values for ^{204}Pb were corrected for the interference of 201 Hg, and isotopic ratios adjusted against the NIST981 data.

Statistical determination of background Pb concentration in soils

Background concentration in soils was estimated using regression analysis of % cumulative frequency curves of log10 metal concentrations from a sample population (Davies, 1983). The lower, linear portion of the curve (Figure 2) is seen as representing a lognormal population derived from uncontaminated samples, and a regression equation can be derived in order to estimate background concentration based on a number of percentile values (16th, 50th, 84th).

Lead concentration data from all samples collected by this study, in addition to those presented by Borgna et al. (2009) and Riccobono et al. (2004) (n=819), were converted to their log10 equivalents and the frequency distribution established for 50 class intervals where optimum class width (log int.) is given by:

$$\text{Log int.} = \frac{\log\left(\frac{\text{maximum concentration}}{\text{minimumconcentration}}\right)}{\text{Number of class intervals}} \qquad \text{Equation 1}$$

The percentage cumulative frequency distribution (F) was calculated and Sinclair's (1974) method was used to resolve the complex curve into its constituent populations. The resulting curves comprise a linear lower portion, representing the 'background' population (B), and a complex curve, derived from samples with above 'background' Pb and Zn content (A). For each point along the linear relationship (B) F was recalculated as F', where:

$$F' = (100 - F) \times \left(\frac{100}{B}\right) \quad \text{Equation 2}$$

Where F is the % cumulative frequency distribution and B is the percentage of the total sample number derived containing 'background' concentrations. The mean and standard deviation of F' are readily derived, with the mean log10 concentration corresponding to 50% cumulative frequency and the anti-log is the geometric mean (XM) of the arithmetic data. For a normally distributed population, 68% lies within ±1 standard deviation so that the standard deviation derived from:

$$0.5 \times (16\text{th percentile} - 84\text{th percentile}) \quad \text{Equation 3}$$

The antilog is the geometric deviation (SM) of the arithmetic data. The highest probable Pb concentration for an unenriched soil is derived from the statistical inference that only 0.14% of the population is likely to lie beyond the range given by XM multiplied by SM^3.

Additional statistical analyses in this study were performed using IBM SPSS Statistics Version 20 and the Solver Function in Microsoft Excel.

4. RESULTS AND DISCUSSION

4.1. Metal concentrations in mine, smelter and industrial waste

Table 1 presents data on metal concentrations in samples taken from unconsolidated mine tailings, smelter slag and industrial waste stored at three locations to the north and east of Mitrovica (Figure 1). In terms of contaminant metal storage, it is estimated that the Zharkov Potok tailings pond holds approximately 9 M tonnes of waste material with Pb and Zn concentrations up to 1500 mg kg^{-1} and 1400 mg kg^{-1}, respectively. The Gorne Polje dumps contain approximately 12 M tonnes of Pb and Zn-rich material covering 50 ha (Frese et al., 2004) and is made up of two sedimentologically distinct waste types. Firstly a pale red, fine sand-size material that comprises the majority of the waste material, and second, a black coarse-sand sized partially-vitreous material. The former is believed to be flotation waste, whilst the latter is believed to be smelter slag. Metal concentrations in the Gornje Polje waste dumps contain between 1700 – 82,000 mg kg^{-}

$^{-1}$ Pb and 3000 – 49,700 mg kg^{-1} Zn. Based upon average metal concentrations and reported waste tonnages, in the Zarkov Potok tailings pond there are ~12,800 tonnes and ~5,700 tonnes of unrecovered Pb and Zn, respectively, and in the Gorne Polje waste dump ~280,000 tonnes and ~42,500 tonnes of unrecovered Pb and Zn, respectively. At the Trepča Industrial Complex, unconsolidated particulate waste from the Zn electrolysis and battery reprocessing plants contains 60-1100 mg kg^{-1} Cd, 11,500-88,000 mg kg^{-1} Zn and 7700-13,600 mg kg^{-1} Pb. A particular issue of concern at both the Gornje Polje and Trepča Industrial Complex waste dumps is the fact that highly metal-contaminated material is being actively delivered into the Sitnica River by sheet wash, gullying and bank erosion processes. In addition this unconsolidated material is subject to wind-blown dispersal of the finer sediment fractions. The significance of this uncontrolled contaminant dispersal is discussed in more detail below.

4.2. PHE concentrations in soils

Minimum, mean and maximum PHE concentrations in the study area are shown in Figure 3. With respect to the entire dataset, maximum and mean concentrations are in the order of Pb>Zn>Cu>Cd. Highest mean and maximum concentrations are generally found in surface soils (0-10 cm) with concentrations reducing with depth. Non-parametric significant difference analysis (Mann Whitney U Test) (Table 2) indicates that a statistically significant difference exists between all PHE levels at 0-10 cm and those at 30-50 cm, predominantly at $\alpha = 0.01$, and between 10-30 cm and 30-50 cm (at $\alpha = 0.01$). There is, however, no significant difference between Pb ($p= 0.4400$) and Cd ($p=0.0980$) levels between 0-10 cm and between 10-30 cm. These data generally indicate that greatest PHE enrichment is present within upper soil profile, importantly, the environment with which human interaction with soils will be greatest (Abrahams, 2002).

To quantify the magnitude of enrichment, PHE concentrations in soils were evaluated using a twofold approach. First, metal concentrations were compared with the latest guideline values developed by the Dutch Ministry for Housing and Spatial Planning (VROM, 2000), which represent a long-established (first used in 1962) and stringent set of quality criteria that are based upon extensive studies of both human and eco-toxicological effects of contaminants (Table 3). Second, given that Pb is the principal contaminant of concern in this study, a statistical approach based on that of Davies (1983) was used to quantify the 'background' Pb concentration in soils collected in the Mitrovica region. Previous studies of metal enrichment in environmental media have highlighted the value and relevance of quantifying concentrations relative to naturally-occurring 'background' concentrations (Hudson-Edwards et al., 1999; Martin, 2004). Using the Davies approach, the threshold Pb concentration for uncontaminated soil (i.e. background) was calculated to be 80 mg kg^{-1} in the Mitrovica region. This value is very close to the Dutch target value (85 mg kg^{-1}, Table 3) and is also in good agreement with Pb concentrations measured at depth

in a 1 m soil profiles at Roma Mahalla (Figure 4), where concentrations of Pb at 50-100 cm depth range from 38-71 mg kg^{-1}. The calculated background value also agrees well with metal concentrations measured in two c. 1.5 m soil profiles to the SW of Mitrovica by Riccobono et al. (2004), with Pb concentrations below 50 cm depth in the two profiles averaging 67 mg kg^{-1} and 134 mg kg^{-1} (Figure 4). Taken together, these data suggest that the calculated threshold of 80 mg kg^{-1} is indicative of uncontaminated soils in the Pb-mineralized region of Mitrovica. Given that mean PHE concentrations at 0-10 cm depth were between 1.5-2.1 and 2.8-4.9 times greater than those at 10-30 cm and 30-50 cm depth, respectively, subsequent analysis of enrichment above threshold values has focused upon data for the upper soil layer (0-10 cm).

There is clear evidence of elevated PHE concentrations within surface soils in the IDP camps (Figure 3). First, maximum Cd, Cu, Pb and Zn concentrations are enriched above Dutch Intervention values by between 1.1 and 10 times. Second, at Osterode and Cesmin Lug mean Cd (4 and 3 mg kg^{-1}, respectively) and Cu (71 and 129 mg kg^{-1}, respectively) concentrations exceed the Dutch target values and mean Pb (1784 and 1230 mg kg^{-1}, respectively) and Zn (1490 and 2100 mg kg^{-1}, respectively) concentrations exceed the higher Dutch intervention values. Third, Pb concentrations in the two camps exceed the 80 mg kg^{-1} 'background' concentration in all samples by between 7 and 64 times. At Bosniak Mahalla (n=20), 100% of samples contained Pb (2450-11000 mg kg^{-1}) and Zn (840-3780 mg kg^{-1}) at concentrations in excess of the Dutch intervention values. Cadmium (0.1-10 mg kg^{-1}) and Cu (20-110 mg kg^{-1}) at Bosniak Mahalla were lower and exceeded Dutch intervention in 40% and 15% of samples, respectively. At Roma Mahalla, PHE concentrations were generally lower than at Bosniak Mahalla and the IDP camps, however, Pb levels in surface soils (26-1000 mg kg^{-1}) were enriched above Dutch target values in 49 % of samples (n=62), with 98% of samples exceeding the less stringent Pb Target value (85 mg kg^{-1}). Furthermore, 98% of samples at Roma Mahalla contained Pb in excess of the calculated background concentration.

Although PHE concentrations at Roma Mahalla, Bosniak Mahalla and the IDP camps are elevated above Dutch environmental guideline values, the enrichment of soils especially by Pb, is widespread across the Mitrovica municipality (Figure 3). This is supported by results from an extensive soil survey (>800 samples) reported by Riccobono et al. (2004) and Borgna et al. (2009), which showed that the mean Pb concentration (973 mg kg^{-1}) exceeded the Dutch Intervention value, and mean Cd (7 mg kg^{-1}), Cu (56 mg kg^{-1}) and Zn (560 mg kg^{-1}) concentrations exceeded Dutch Target values across a 350 km^2 area in northern Kosovo that included Mitrovica.

4.3. PHE concentrations in house dust

Maximum PHE concentrations were found in samples collected from the IDP camps (Table 4), with maximum PHE concentrations in the order of Pb>Zn>Cu>Cd. Mining and smelting activity have often been identified as key industrial sources of contaminated house dust (Hwang et al., 1997; Bosso and Enzweiler, 2008), but wind-blown transfer of metals from contaminated soils may also act as a significant source (Layton and Beamer, 2009). At the IDP camps, Pb concentrations in house dust (mean = 4537 mg kg^{-1}), are an order of magnitude higher than at Roma Mahalla and are higher even than the maximum surface soil Pb concentration found in these sites (3600 mg kg^{-1}). To achieve Pb levels in household dust between 5500 and 5900 mg kg^{-1}, the source material supplying the dust is most likely to have equivalent or higher concentrations.

4.4. Lead concentrations in scalp hair

Human exposure to metals can be measured in different tissues and biological fluids (Gulson, 2008), however, hair and blood have been the most widely used biological monitors (Torrente et al., 2005). Whilst blood tends to reflect recent exposure to metals, hair provides a record of longer-term exposure (Bencko, 1995). Lead levels measured in scalp hair samples collected from occupants of the Osterode and Cesmin Lug IDP camps ranged between 25 and 130 mg kg^{-1} (Figure 5). The highest scalp hair Pb concentrations (120 and 130 mg kg^{-1}) were found in residents of the Cesmin Lug camp; this camp also had a higher mean Pb concentration (90 mg kg^{-1}) than the Osterode camp (46 mg kg^{-1}). These concentrations are at the lower end of the range measured previously by Runow (2005b) but are generally higher than Pb levels reported by a number of previous studies around the world (Figure 5). Of particular significance is the fact that scalp hair Pb levels in the children and young people living in the Osterode and Cesmin Lug camps are often higher than published levels for adults who have been exposed to Pb via their occupational activities (Wang et al., 2009). Given that metal levels in scalp hair are indicative of long-term exposure (Bencko, 1995), the data suggest that residents of both camps have been subject to sustained Pb exposure for a prolonged period of time.

4.5. Isotopic fingerprinting of Pb

Potential anthropogenic sources of Pb relate primarily to metallurgical industries within the Mitrovica region, namely; historical release of Pb-rich aerosols from the operation of the Zveçan Pb/Zn smelter, wind-blown dispersal of Pb-rich waste from the Gornje Polje tailings dump and the dispersal of wind-blown material from the Zarkov Potok and Zn electrolysis plant and Battery Factory waste dumps. Finally, the influence of Pb released from the combustion of leaded petrol represents an additional, and potentially longer-lasting, source of Pb. Despite being phased out from the 1990s, the continued presence in the environment of Pb

from leaded petrol combustion has been noted by a number of previous studies (Flegal et al., 2010; Soto-Jimenez et al., 2008).

Lead isotopic signatures ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios) for these sources (Figure 6) indicate that these form a linear trend with the signatures for leaded petrol and bedrock (indicative of geogenic Pb isotope signatures) forming the end members. Of the sources of metallurgical waste identified in Mitrovica, the Gornje Polje smelter slag has the lowest $^{206}Pb/^{207}Pb$ and highest $^{208}Pb/^{206}Pb$ ratios, with the remaining potential sources falling between these and bedrock (Figure 6 inset). Hierarchical cluster analysis was used to identify which potential sources (n=7) could be differentiated from each other based upon their $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios with cluster membership determined for two to six clusters inclusive (Table 5). Results indicate that as the number of clusters is reduced, the sources that continue to demonstrate significantly different Pb isotope signatures are Gornje Polje smelter slag and petrol combustion. This indicates that the vitrified material present on the Gornje Polje dump, identified as smelter slag, has a statistically different Pb isotopic signature than other potential sources associated with large-scale metallurgical industry in Mitrovica. The smelter slag has a density of c. 3027 kg m^3, which is higher than the normal range for, for example, soils (1000-2000 kg m^3) identified by Donahue and Miller (1990), and would at least inhibit the dispersal of this material by wind from the Gornje Polje dump. This suggests that the presence of smelter slag isotopic ratios across the city of Mitrovica is the result of Pb-bearing aerosol dispersal originating from the Zveçan smelter during its time of operation, rather than dispersal of stored smelter slag. What cannot be ruled out, however, is the subsequent remobilization of Pb with this isotopic signature from soils and the redistribution and deposition of this material (Laidlaw and Filippelli, 2008).

For IDP surface soils, house dust and scalp hair, ratios of $^{206}Pb/^{207}Pb$ (1.186-1.191) are generally lower and $^{208}Pb/^{206}Pb$ ratios (2.074-2.085) generally higher than those found in flotation waste, Zarkov Potok mine tailings, Zn electrolysis waste and bedrock (Figure 7). The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios for IDP surface soils, house dust and scalp hair plot in closer proximity to the Gornje Polje smelter slag ($^{206}Pb/^{207}Pb$ = 1.187-1.188 and $^{208}Pb/^{206}Pb$ = 2.076-2.079). The greatest range in $^{206}Pb/^{207}Pb$ (1.188-1.195) and $^{208}Pb/^{206}Pb$ ratios (2.064-2.087) is present in surface soils from Bosniak Mahalla, which includes the highest and lowest values for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$, respectively.

A mixing model (c.f. Miller et al., 2007) was used to quantify the contributions of potential anthropogenic and geogenic sources to the Pb load found within soils (0-10 cm and 30-50 cm depth) and dust from Mitrovica. Sources were defined as: Gornje Polje (both smelter slag and flotation waste), leaded petrol, the Zarkov Potok tailings pond, Zn electrolysis waste, Battery Factory waste and bedrock. Leaded petrol

combustion is defined as a potential source given the acknowledged continued presence of Pb in the environment post phasing out of tetra-ethyl Pb additives (Dunlap et al., 2008). Bedrock is included to identify potential geogenic inputs from the weathering of bedrock (Erel et al., 1997).

The principles of the mixing model approach have been described by Yu and Oldfield (1989) and Collins et al. (1997), however in short the approach utilises the following equation:

$$bj = \sum \frac{m}{i} = 1X_i\, a_{ij} \qquad \text{(Equation 4)}$$

where *bj* (j=1,2,3…, n) are *n* independent Pb isotope ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios) of a soil or dust sample composed of *m* distinct source materials, *aij* (i=1,2,3…,*m*) are the corresponding Pb isotope ratios of the *i*th source materials and *xi* being the proportion if the *i*th source in the sediment. Given values of *bj* and *aij*, a series of *n* linear equations were optimized using the Solver function in Microsoft Excel to quantify the contributions of the five sources identified. Two important constraints are that all source proportions must be non-negative (Equation 5) and source proportions must sum to unity (Equation 6).

$$X_i = \geq 0 \qquad \text{(Equation 5)}$$

$$\sum_i^m = 1X_i = 1 \qquad \text{(Equation 6)}$$

The validity of the mixing model results was assessed by comparing the measured parameter values in the soil mixture with the values predicted in the optimization of the linear equations (Equation 7). This assessment (c.f. Miller et al., 2007) quantifies relative errors and indicates whether the mixing model generates an acceptable prediction of the fingerprinting properties. Errors for five iterations of the mixing model (one per sample group) ranged from 0.01-0.07%.

$$\%\, error = \sqrt{\frac{\left(\sum_{i=1}^{m}\left(bi - \sum_{j=1}^{n} a_{ij}x_j\right)\right)^2}{\sum_{i=1}^{m}(b_i)^2}} \times 100 \qquad \text{(Equation 7)}$$

4.6. Pb contribution to soil and house dust

Mixing model results (Table 6) indicate that the dominant source of Pb in surface soils (0-10 cm depth) and house dust from across Mitrovica is smelter slag from the Gornje Polje dump. The mean contribution is highest for surface soils in the IDP camps (92%), however samples collected over a wider spatial area in Mitrovica are still predicted to contain 67-91% Pb from the smelter slag. The importance of this material as

a source over a large spatial area further indicates that this material should be viewed as an analogue for historical atmospheric emissions of Pb from the Zveçan– smelter and its subsequent deposition across Mitrovica. The mixing model indicates that up to 29% (in the case of surface soil samples collected at Bosniak Mahalla) of Pb originates from the flotation waste stored at Gornje Polje. Given the unconsolidated nature of this material, it is believed that the presence of Pb sourced from Gornje Polje reflects the effects of wind-blown dispersal and deposition (Csavina et al., 2011). Across all surface soil samples for which the mixing model was run, Gornje Polje smelter slag and flotation waste in combination account for up to 52-99% of Pb (mean of 82%); in IDP camp surface soils these two sources together account for an average of 93% of Pb. Geogenic inputs to surface soils (Table 6) are highest in Bosniak Mahalla (<1-29%) and Roma Mahalla (<1-14%) but are predicted to contribute less Pb in the IDP camp surface soils or those in wider Mitrovica. Inputs of Pb from petrol combustion are generally low across all surface soil samples (<1-10%), as are those from the Zarkov Potok tailings pond (<1-11%), Zn electrolysis waste (<1-22%) and Battery Factory waste (<1-23%) to the east of Mitrovica.

As noted earlier, the Gornje Polje smelter slag is interpreted as representative of the Pb isotopic signature of emissions from the Zveçan smelter during it period of operation. Given that (i) soils in Mitrovica have a very similar isotopic signature to the Gornje Polje smelter waste, (ii) the coarse mean grain size of the waste (500-2000 μm) effectively prevents deflation and dispersal of this material by wind, and (iii) the Zveçan smelter closed in 2000, it is probable that the elevated Pb concentrations seen in surface soils across Mitrovica are the result of aerosol contamination dispersed prior to 2000 when the Zveçan smelter was operational. Whilst continued inputs from other sources, such as flotation and Zn electrolysis waste cannot be discounted (Table 6), Pb isotopic evidence suggests that, at the larger spatial scale, presently active sources are supplying relatively small amount of Pb to surface soils in comparison to historical emissions.

Interestingly, mixing model results for deeper soils (30-50 cm) indicate that less Pb is associated with the Gornje Polje smelter slag (<1-74 %) than for surface soils (Table 6). In addition, whilst there are modelled contributions from other anthropogenic sources, there is a generally greater proportion of Pb in deeper soils associated with bedrock (4-99 %) than for surface soils. Across the whole sample set, these deeper soils have been shown to contain lower amounts of Pb (mean of 767 mg kg^{-1}) compared to soils from 0-10 cm depth (mean of 2940 mg kg^{-1}). Together, the lower contributions from the dominant Pb source identified in Mitrovica, and lower Pb concentrations, suggest that soils at 30-50 cm depth have been relatively isolated from contamination caused notably through the airborne deposition of Pb as seen particularly in surface soils. However, these deeper soils still contain Pb concentrations up to 55 times above calculated background concentrations and modelled to contain 1-96 % of Pb from anthropogenic sources. In combination, this

suggests that there has either been a down profile movement of Pb associated with pedogenic processes, and/or these soils were once exposed at the surface and have since been buried.

Much like surface soils, the mixing model suggests the dominant source of Pb in house dust is the Gornje Polje smelter slag (78-99 %), interpreted here as reflecting smelter emissions. However, in the case of house dust it is important to note that Pb in this material may well not reflect the primary product of smelter emissions but may well be Pb originally deposited onto soils and then resuspended through the formation of dust from these soils and deposited into the sampled houses (Laidlaw et al., 2014).

The mixing model results have highlighted the importance of anthropogenic sources in the provenance of Pb in soils and house dust. However, it must be noted that additional, unidentified sources may have contributed, or continue to contribute, to the Pb present in samples collected from Mitrovica. Whilst it is unlikely that additional sources would be of greater importance than emissions from the Zveçan smelter at the larger spatial scale, it is possible that unidentified sources may contribute smaller amounts of Pb. At the larger spatial scale, Pb may be sourced from coal combustion (Walraven et al., 2013); however Pb content in European lignite coals, the dominant coal type in Kosovo, are <14 mg kg^{-1} (Kortenski and Sotirov, 2002), suggesting that this would be a very minor input, certainly compared to smelter waste. Other potential sources of Pb, which may be relevant on a site-specific basis, have been identified by previous studies as leaded paint (e.g. Brokbartold et al., 2013; Clark and Knudsen, 2013), plumbing and pipework (e.g. Gidlow, 2004) and emissions from various metallurgical other industries (e.g. Zhang et al., 2009). Finally, Prathumratana et al. (2008) have also suggested the practice of battery smelting by local populations may account for some Pb release at the smaller spatial scale in Mitrovica.

4.7. Pb contribution to scalp hair

Mixing model results (Table 7) suggest that, based upon $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios, 89-94% of Pb found in scalp hair from persons then living in IDP camps is predicted to have been sourced from Gornje Polje smelter slag, interpreted as representing historical smelter emissions. Smaller contributions of Pb are predicted from petrol combustion (<1-3 %), Gornje Polje flotation waste (<1-2 %) and Zn electrolysis waste stored to the SE of the city (6-8 %). There are, however, no statistically significant correlations between the concentrations of Pb measured in scalp hair and the modelled percentage contributions from Gornje Pole smelter slag (r=0.21), flotation waste (r=0.08), petrol combustion (r=0.29) or Zn electrolysis waste (r=0.08). This indicates that Pb source is not an accurate predictor of Pb concentration. Indeed, it is probable that the degree of Pb uptake will vary from person to person, influenced by the bioavailability of Pb (Boisa et al.,

2013; Huang et al., 2014) and the nature of the exposure mechanism and human behaviour (Pirkle et al., 1998).

Given that the Zveçan smelter closed 10 years prior to sampling, it is unlikely that the Pb in scalp hair will reflect exposure via direct inhalation of Pb-bearing smelter emissions. What is more likely is that, given the substantial contribution of historical smelter emissions to the Pb load in surface soils and house dust (Table 6), human Pb exposure has occurred through exposure to contaminated soils and house dust. Exposure can occur through dust inhalation (Lau et al., 2014) and deliberate and non-deliberate ingestion of soil and dust (Moya et al., 2004). Modelling Pb contribution to scalp hair using IDP camp soils (mean isotope ratios of $^{206}Pb/^{207}Pb = 1.188$ and $^{208}Pb/^{206}Pb = 2.080$) as a source instead of the Gornje Polje smelter slag, suggests predicted Pb contributions of 68-87 % from these soils. Performing the same analysis using house dust as a source (mean isotope ratios of $^{206}Pb/^{207}Pb = 1.189$ and $^{208}Pb/^{206}Pb = 2.077$), predicts an 86-88 % contribution to Pb in scalp hair. These contributions from soils and house dust are generally similar (means of 82 and 87%, respectively) and are similar to those predicted for Gornje Polje smelter slag (mean of 91 %). In combination with the similar isotopic signatures for these materials, this further suggests that exposure to Pb from the Zveçan smelter has been non-direct and through a potential combination of interaction with surface soil and house dust.

4.8. Implications for environmental management

Soils, particularly surface soils, and house dust in Mitrovica are severely contaminated with a range of PHEs, notably Pb. Lead isotope analysis has indicated that point sources within the city have contributed varying amounts of Pb soils and house dust. Some of these sources, such as deposits of flotation waste at Gornje Polje and Zn electrolysis waste, which have contributed up to 28 % and 22 %, respectively to Pb present within soils, could be considered to be presently 'active' point sources. That is, these are unconsolidated deposits, which are susceptible to remobilization of material. However, mixing model data indicate that the most significant contributor has been historical emissions from the Zveçan Pb/Zn smelter. This point source is no-longer active, but has played the major role in Pb loading to the environment in Mitrovica.

The challenge for environmental management and remediation is that the presence of elevated Pb particularly in surface soils, constitutes a potentially spatially extensive diffuse source of Pb both to the environment (through physical remobilization, for example via dust generation), and to local populations. Whilst not without challenges, point sources such as Gornje Polje can be remediated to reduce the potential for Pb (and other PHE) release into the environment, through measures such as capping and revegetation

(Tordoff et al., 2000). However, reducing the risk posed by diffuse sources, such as Pb in soils, is much more difficult, particularly given the spatially extensive PHE enrichment in Mitrovica and the surrounding region.

5. CONCLUSIONS

This study has demonstrated the extent and severity of PHE enrichment in surface soils and house dust that has occurred within the Mitrovica urban area; a location of intensive former metallurgical activity. Furthermore, Pb concentrations in scalp hair collected by this study, and in blood by others, indicate that populations within Mitrovica have suffered from Pb uptake to levels rarely reported elsewhere in the scientific literature. Lead isotopes have proven to be a powerful tool for provenancing the source of Pb in soils and human scalp hair through the application of a mixing model. Results demonstrate that Pb present within surface soils is likely to be dominantly-sourced from the deposition of Pb-bearing aerosols from the historical operation of the Zvecan smelter. Deeper soils, which demonstrate lower PHE concentrations in general, show greater Pb loading from geogenic inputs compared to surface soils. With respect to Pb present in scalp hair, whilst Pb isotope analysis suggests the original source to be from emissions from the Zvecan smelter, it is believed uptake to humans, and subsequent presence in scalp hair, is as a result of ingestion and inhalation of Pb-contaminated soils and house dust.

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Figure Captions

Figure 1. Mitrovica study area showing the principal contaminant sources and sampling site locations.

Figure 2. Cumulative frequency curve used to determine the background populations for Pb: Curve 1 is the frequency plot of log10 Pb values in soils, Curve 2 is the frequency curve for F' (cf. Davies, 1983) at the lower "background" threshold, and Curve 3 is the frequency curve for F' at the upper "severely contaminated" threshold.

Figure 3. Minimum, mean and maximum PHE concentrations in Mitrovica soils.

Figure 4. Lead concentrations measured in soil profiles at Roma Mahalla (this study) and at two sites to the SW of Mitrovica (Riccobono et al., 2004).

Figure 5. Range and mean Pb concentrations in human scalp hair of inhabitants of the IDP camps, Mitrovica and data reported in the literature. The horizontal dashed line is the mean value determined by this study. Data from: [1]this study, [2]Runow (2005a), [3] Wang et al. (2009), [4]Hornos-Carneiro et al. (2011), [5] Kazi et al. (2014), [6]Barton et al. (2000), [7]Rodrigues et al. (2008), [8]Michalak et al. (2014), [9]Morton et al. (2002), [10,12]Rodushkin and Axelsson (2000), [11]Varrica et al. (2014).

Figure 6. Ratios of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ determined in metallurgical waste and bedrock from Mitrovica and for European tetra-ethyl Pb produced by the Octel Company between 1980 and 1995 (Veron et al., 1999)

Figure 7. Ratios of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ determined in surface soils, house dust and scalp hair in Mitrovica.

Table 1. Minimum, maximum and mean (in parenthesis) metal concentrations (mg kg^{-1}) in mine, smelter and industrial waste in Mitrovica. See Figure 1 for sample site locations.

	Cd	**Cu**	**Pb**	**Zn**
Zharkov Potok tailings (n=3)	1-5 (3)	160-550 (400)	1270-1570 (1420)	230-1400 (630)
Gorne Polje waste (n=5)	1-4 (3)	200-28,000 (12600)	3400-50,000 (23400)	1700-82,600 (35500)
Trepca Industrial Complex, Zn electrolysis waste (n=3)	62-1200 (710)	2690-7390 (5640)	190-33,100 (13690)	11,500-135,400 (112960)
Trepca Industrial Complex, battery & chemical factory waste (n=1)	13	400	1600	1700

Table 2. Mann-Whitney U test p values for significant difference between PHE concentrations at different soil depths. Italicized values are significant at $\alpha = 0.05$ and those in bold at $\alpha = 0.01$.

	Cd	**Cu**	**Pb**	**Zn**
0-10 cm and 10-30 cm	0.0980	*0.0121*	0.4400	*0.0144*
0-10 cm and 30-50 cm	**0.0000**	**0.0000**	**0.0000**	**0.0000**
10-30 cm and 30-50 cm	**0.0001**	**0.0000**	**0.0000**	**0.0000**

Table 3. Dutch Soil remediation standards for various metals (concentrations in mg kg^{-1} dry weight). Data from VROM (2000).

	Cd	**Cu**	**Pb**	**Zn**
Target	0.8	36	85	140
Intervention	12	190	530	720

Table 4. Range and (in parentheses) PHE concentration (mg kg^{-1}) in house dust collected in Roma Mahalla and the IDP camps.

	Cd	**Cu**	**Pb**	**Zn**
Roma Mahalla	1-6	13-60	60-650	60-460
(n=3)	(4)	(43)	(440)	290)
IDP camps	5-14	220-360	550-5900	2200-4630
(n=4)	(8)	(293)	(4537)	(3080)

Table 5. Cluster analysis output

	Number of clusters				
Source	6	5	4	3	2
Zarkov Potok	1	1	1	1	1
Gornje Polje smelter slag	2	2	2	2	1
Gornje Polje flotation waste	3	3	3	1	1
Zn electrolysis waste	4	3	3	1	1
Battery Factory waste	5	4	1	1	1
Bedrock	1	1	1	1	1
Petrol combustion	6	5	4	3	2

Table 6. Range and mean (in parentheses) percentage contributions of Pb to soils and house dust from potential sources in Mitrovica.

	Gornje Polje smelter slag	Gornje Polje flotation waste	Zarkov Potok	Zn electrolysis waste	Petrol combustion	Battery Factory waste	Bedrock
	Surface soils (0-10 cm)						
Bosniak Mahalla (n=14)	24-99 (78)	<1-28 (8)	<1	<1-5 (<1)	<1-6 (2)	<1-23 (5)	<1-29 (8)
Roma Mahalla (n=6)	52-99 (84)	<1-10 (2.5)	<1-11 (2)	<1-22 (6)	<1	<1	<1-14 (5)
IDP Camps (n=6)	91-93 (92)	<1-2 (<1)	<1	6-8 (7)	<1-1 (<1)	<1	<1
Mitrovica soils (n=10)	67-91 (78)	<1-6 (4)	<1-2 (<1)	6-12 (10)	<1-4 (2)	<1-11 (6)	<1-3 (<1)
	Deep sub-surface soils (30-50 cm depth)						
Mitrovica soils (n=10)	<1-71 (52)	<1-9 (3)	<1-16 (6)	<1-12 (8)	<1-9 (2.5)	<1	4-99 (27)
	House dust						
Mitrovica (n=6)	78-99 (87)	<1-3 (1)	<0-2 (<1)	<1-16 (10)	<1	<1	<1-3 (1)

Table 7. Range and mean (in parentheses) percentage contributions of Pb in scalp hair from potential sources in Mitrovica.

	Gornje Polje smelter slag	Gornje Polje flotation waste	Zarkov Potok	Zn electrolysis waste	Petrol combustion	Battery Factory waste	Bedrock
Scalp hair (n=10)	89-94 (92)	<1-2 (<1)	<1	6-8 (6.5)	<1-4 (1)	<1	<1

References

Abrahams, P.W., 2002. Soils: their implications to human health. Science of the Total Environment 291, 1-32.

Alfonso, S., Grousset, F., Masse, L., Tastet, J.-P., 2001. A European lead isotope signal recorded from 6000 to 300 years BP in coastal marshes (SW France). Atmospheric Environment 35, 3595-3605.

Allan, R., 1997. Introduction: Mining and metals in the environment. Journal of Geochemical Exploration 58, 95-100.

Bacon, J.R., 2002. Isotopic characterisation of lead deposited 1989-2001 at two upland Scottish locations. Journal of Environmental Monitoring 4, 291-299.

Bacon, J.R., Dinev, N.S., 2005. Isotopic characterisation of lead in contaminated soils from the vicinity of a non-ferrous metal smelter near Plovdiv, Bulgaria. Environmental Pollution 134, 247-255.

Barman, S.C., Kisku, G.C., Bhargava, S.K., 1999. Accumulation of heavy metals in vegetables, pulse and wheat grown in fly ash amended soil. Journal of Environmental Biology 20, 15-18.

Baron, S., Le-Carlier, C., Carignan, J., Ploquin, A., 2009. Archaeological reconstruction of medieval lead production: Implications for ancient provenance studies and palaeopollution tracing by Pb isotopes. Applied Geochemistry 24, 2093-2101.

Barton, H., Zachyieja, Z., D'Ilio, S., Caroli, S., 2000. Application of routine estimation of Pb isotopic ratios by inductively coupled plasma mass spectrometry for studying the Pb origin in hair of children living in polluted areas. A pilot study. Microchemical Journal 67, 21-30.

Behrami, S., Bajraktari, F., Zogaj, N., 2008. Ground water pollution in Mitrovica and surroundings, in: Morell, M., Popovska, C., Morell, O., Stojov, V., Kostoski, G., Dimitrov, D., Drobot, R., Radic, Z., Selenica, A. (Eds.), BALWOIS 2008: Conference on Water Observation and Information System for Decision Support. Ministry of Education and Science, Republic of Macedonia, Ohrid, Republic of Macedonia, pp. 1-5.

Bencko, V., 1995. The use of human hair as a biomarker in the assessment of exposure in occupational and environmental setting. Toxicology 101, 29-39.

Bird, G., 2011. Provenancing anthropogenic Pb within the fluvial environment: Developments and challenges in the use of Pb isotopes. Environment International 37, 802-819.

Bird, G., Brewer, P.A., Macklin, M.G., Nikolova, M., Kotsev, T., Mollov, M., Swain, C., 2010a. Contaminant-metal dispersal in mining-affected river catchments of the Danube and Maritsa drainage basins, Bulgaria. Water Air and Soil Pollution 206, 105-127.

Bird, G., Brewer, P.A., Macklin, M.G., Nikolova, M., Kotsev, T., Mollov, M., Swain, C., 2010b. Quantifying sediment-associated metal dispersal using Pb isotopes: application of binary and multivariate mixing models in the Maritsa catchment, Bulgaria. Environmental Pollution 158, 2158-2169.

Bird, G., Brewer, P.A., Macklin, M.G., Serban, M., Balteanu, D., Driga, B., Zaharia, S., 2008. River system recovery following the Novaţ-Roşu tailings dam failure, Maramureş County, Romania. Applied Geochemistry 23, 3498-3518.

Bird, G., Macklin, M.G., Brewer, P.A., Zaharia, S., Balteanu, D., Driga, B., Serban, M., 2009. Heavy metals in potable groundwater of mining-affected river catchments, northwestern Romania. Environmental Geochemistry and Health 31, 741-758.

Boisa, N., Bird, G., Brewer, P.A., Dean, J.R., Entwistle, J.A., Kemp, S.J., Macklin, M.G., 2013. Potentially harmful elements (PHEs) in scalp hair, soil and metallurgical wastes in Mitrovica, Kosovo: The role of oral bioaccessibility and mineralogy in human PHE exposure. Environment International 60, 56-70.

Borgna, L., Di Lella, L.A., Nannoni, F., Pisani, A., Pizzetti, E., Protano, G., Riccobono, F., Rossi, S., 2009. The high contents of lead in soils of northern Kosovo. Journal of Geochemical Exploration 101, 137-146.

Bosso, S.T., Enzweiler, J., 2008. Bioaccessible lead in soils, slag, and mine wastes from an abandoned mining district in Brazil. Environmental Geochemistry and Health 30, 219-229.

Brokbartold, M., Temminghoff, E.J.M., Weng, L.P., Marschner, B., 2013. Unique characteristics of Pb in soil contaminated by red lead anti-corrosion paint. Soil & Sediment Contamination 22, 839-855.

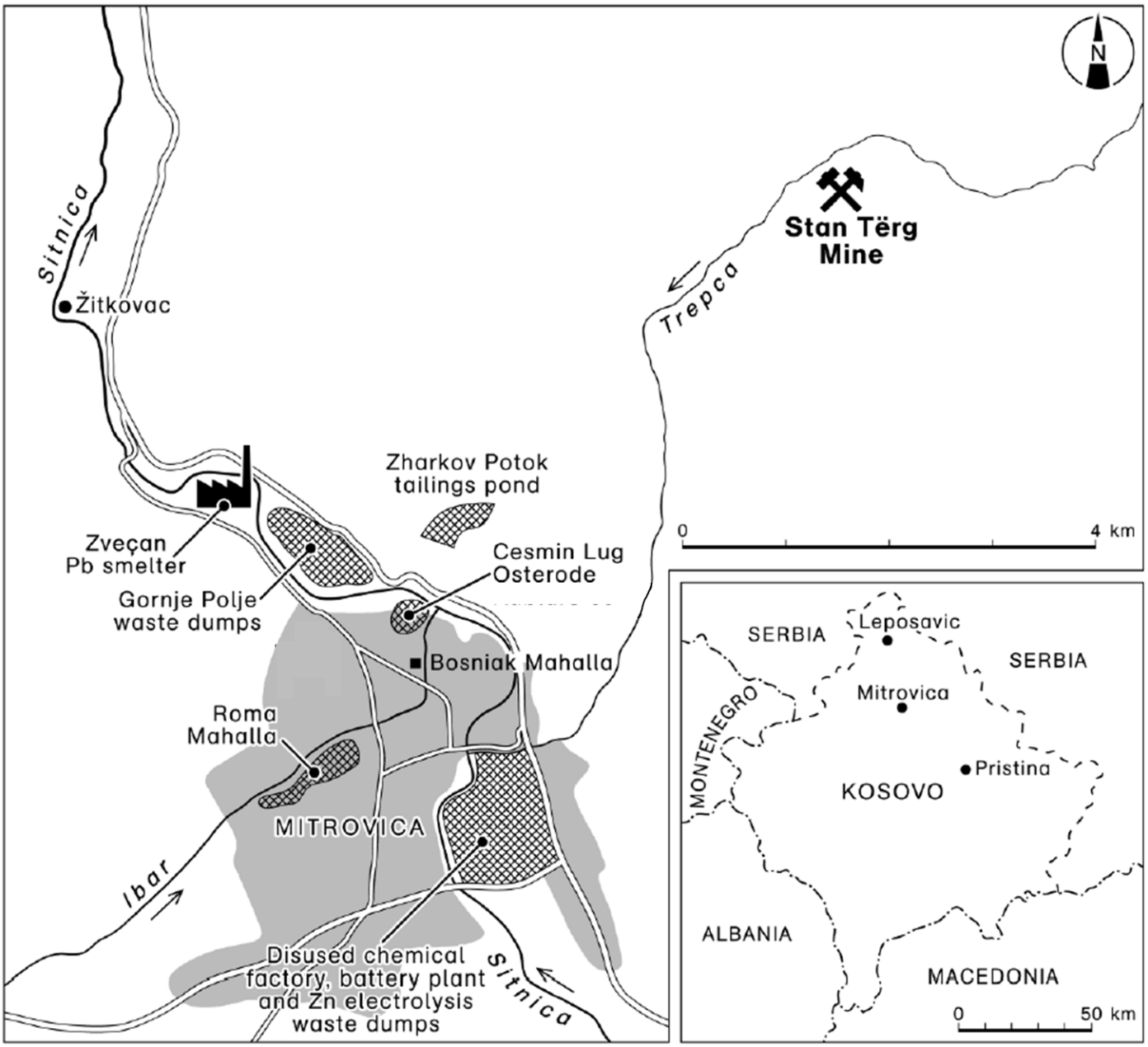
Clark, J.J., Knudsen, A.C., 2013. Extent, characterization, and sources of soil lead contamination in small-urban residential neighborhoods. Journal of Environmental Quality 42, 1498-1506.

Collins, A.L., Walling, D.E., Leeks, G.J.L., 1997. Fingerprinting the origin of fluvial suspended sediments in larger river basins: combining assessment of spatial provenance and source type. Geografiska Annaler 79, 239-254.
Csavina, J., Landázuri, A., Wonaschütz, A., Rine, K., Rheinheimer, P., Barbaris, B., Conant, W., Sáez, A., Betterton, E., 2011. Metal and metalloid contaminants in atmospheric aerosols from mining operations. Water, Air, & Soil Pollution 221, 145-157.
Davies, B.E., 1983. A graphical estimation of the normal lead content of some British soils. Geoderma 29, 67-75.
Dennis, I.A., Coulthard, T.J., Brewer, P.A., Macklin, M.G., 2009. The role of floodplains in attenuating contaminated sediment fluxes in formerly mined drainage basins. Earth Surface Processes and Landforms 34, 453-466.
Doe, B.R., 1970. Lead Isotopes. Springer, Berlin.
Donahue, R.L., Miller, R.W., 1990. Soils: An Introduction to Soils and Plant Growth, 6th ed. Prentice-Hall.
Dunlap, C.E., Alpers, C.N., Bouse, R., Taylor, H.E., Unruh, D.M., Flegal, A.R., 2008. The persistence of lead from past gasoline emissions and mining drainage in a large riparian system: Evidence from lead isotopes in the Sacramento River, California. Geochimica Et Cosmochimica Acta 72, 5935-5948.
El Khalil, H., El Hamiani, O., Bitton, G., Ouazzani, N., Boularbah, A., 2008. Heavy metal contamination from mining sites in South Morocco: Monitoring metal content and toxicity of soil runoff and groundwater. Environmental Monitoring and Assessment 136, 147-160.
Erel, Y., Veron, A., Halicz, L., 1997. Tracing the transport of anthropogenic lead in the atmosphere and in soils using isotope ratios. Geochimica Et Cosmochimica Acta 61, 4495-4505.
Ettler, V., Mihaljevič, M., Šebek, O., Molek, M., Grygar, T., Zeman, J., 2006. Geochemical and Pb isotopic evidence for sources and dispersal of metal contamination in stream sediments from the mining and smelting district of Pribram, Czech Republic. Environmental Pollution 142, 409-417.
Factor-Litvak, P., Wasserman, G., Kline, J.K., Graziano, J., 1999. The Yugoslavia prospective study of environmental lead exposure. Environmental Health Perspectives 107, 9-15.
Flegal, A.R., Gallon, C., Hibdon, S., Kuspa, Z.E., Laporte, L.F., 2010. Declining-but persistent-atmospheric contamination in Central California from the resuspension of historic leaded gasoline emissions as recorded in the Lace Lichen (Ramalina menziesii Taylor) from 1892 to 2006. Environmental Science and Technology 44, 5613-5618.
Frese, S.D., Klitgaard, R., Pedersen, E.K., 2004. Environmental Management in Kosovo: Heavy Metal Emission from Trepca. Institut for Miljø, Teknologi og Samfund, Roskilde, p. 143.
Fytianos, K., Katsianis, G., Triantafyllou, P., Zachariadis, G., 2001. Accumulation of heavy metals in vegetables grown in an industrial area in relation to soil. Bulletin of Environmental Contamination and Toxicology 67, 423-430.
Geraldes, M.C., Paula, A.H., Godoy, J.M., Valeriano, C.M., 2006. Pb isotope signatures of sediments from Guanabara Bay, SE Brazil: evidence for multiple anthropogenic sources. Journal of Geochemical Exploration 88, 384-388.
Gidlow, D.A., 2004. Lead toxicity. Occupational Medicine-Oxford 54, 76-81.
Gulson, B., 2008. Stable lead isotopes in environmental health with emphasis on human investigations. Science of the Total Environment 400, 75-92.
Hornos Carneiro, M.F., Moresco, M.B., Chagas, G.R., de Oliveira Souza, V.C., Rhoden, C.R., Barbosa, F., Jr., 2011. Assessment of Trace Elements in Scalp Hair of a Young Urban Population in Brazil. Biological Trace Element Research 143, 815-824.
Houtermann, F.G., 1946. The isotopic abundances in natureal lead and the age of uranium. Naturwissenschaften 33, 185-186.
Huang, M., Wang, W., Chan, C.Y., Cheung, K.C., Man, Y.B., Wang, X., Wong, M.H., 2014. Contamination and risk assessment (based on bioaccessibility via ingestion and inhalation) of metal(loid)s in outdoor and indoor particles from urban centers of Guangzhou, China. The Science of the total environment 479-480, 117-124.
Hudson-Edwards, K.A., Macklin, M.G., Finlayson, R., Passmore, D.G., 1999. Mediaeval lead pollution in the River Ouse at York, England. Journal of Archaeological Science 26, 809-819.
Hurkamp, K., Raab, T., Volkel, J., 2009. Lead pollution of floodplain soils in a historic mining area-age, distribution and binding forms. Water Air and Soil Pollution 201, 331-345.

Hutchinson, S.M., Rothwell, J.J., 2008. Mobilization of sediment-associated metals from historical Pb working sites on the River Sheaf, Sheffield, UK. Environmental Pollution 155, 61-71.
Hwang, Y.H., Bornschein, R.L., Grote, J., Menrath, W., Roda, S., 1997. Environmental arsenic exposure of children around a former copper smelter site. Environmental Research 72, 72-81.
Ip, C.C.M., Li, X.D., Zhang, G., Wai, O.W.H., Li, Y.S., 2007. Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. Environmental Pollution 147, 311-323.
Jung, M.C., Thornton, I., 1996. Heavy metal contamination of soils and plants in the vicinity of a lead-zinc mine, Korea. Applied Geochemistry 11, 53-59.
Kazi, T.G., Shah, F., Shaikh, H.R., Afridi, H.I., Shah, A., Naeemullah, Arain, S.S., 2014. Exposure of lead to mothers and their new born infants, residents of industrial and domestic areas of Pakistan. Environmental Science and Pollution Research 21, 3021-3030.
Komárek, M., Chrastnỳ, V., Štíchová, J., 2007. Metal/metalloid contamination and isotopic composition of lead in edible mushrooms and forest soils originating from a smelting area. Environment International 33, 677-684.
Komárek, M., Ettler, V., Chrastny, V., Mihaljevič, M., 2008. Lead isotopes in environmental sciences: a review. Environment International 34, 562-577.
Kortenski, J., Sotirov, A., 2002. Trace and major element content and distribution in Neogene lignite from the Sofia Basin, Bulgaria. International Journal of Coal Geology 52, 63-82.
Laidlaw, M.A.S., Filippelli, G.M., 2008. Resuspension of urban soils as a persistent source of lead poisoning in children: A review and new directions. Applied Geochemistry 23, 2021-2039.
Laidlaw, M.A.S., Zahran, S., Pingitore, N., Clague, J., Devlin, G., Taylor, M.P., 2014. Identification of lead sources in residential environments: Sydney Australia. Environmental Pollution 184, 238-246.
Lamb, M.R., Janevic, T., Liu, X., Cooper, T., Kline, J., Factor-Litvak, P., 2008. Environmental lead exposure, maternal thyroid function, and childhood growth. Environmental Research 106, 195-202.
Lau, W.K.Y., Liang, P., Man, Y.B., Chung, S.S., Wong, M.H., 2014. Human health risk assessment based on trace metals in suspended air particulates, surface dust, and floor dust from e-waste recycling workshops in Hong Kong, China. Environmental Science and Pollution Research 21, 3813-3825.
Layton, D.W., Beamer, P.I., 2009. Migration of contaminated soil and airborne particulates to indoor dust. Environmental Science & Technology 43, 8199-8205.
Lewin, J., Macklin, M.G., 1987. Metal mining and floodplain sedimentation in Britain, in: Gardiner, V. (Ed.), International Geomorphology 1986: Proceedings of the First International Conference on Geomorphology. John Wiley and Sons, Chichester, pp. 1009-1027.
Loiacono, N.J., Graziano, J.H., Kline, J.K., Popovac, D., Ahmedi, X., Gashi, E., Mehmeti, A., Rajovic, B., 1992. Placental cadmium and birth-weight in women living near a lead smelter. Archives of Environmental Health 47, 250-255.
Martin, C.W., 2004. Heavy metal storage in near channel sediments of the Lahn River, Germany. Geomorphology 61, 275-285.
Michalak, I., Woowiec, P., Chojnacka, K., 2014. Determination of exposure to lead of subjects from southwestern Poland by human hair analysis. Environmental Monitoring and Assessment 186, 2259-2267.
Mihaljevič, M., Ettler, V., Šebek, O., Strnad, L., Chrastnỳ, V., 2006. Lead isotope signatures of wine and vineyard soils - tracers of lead origin. Journal of Geochemical Exploration 88, 130-133.
Miller, J.R., Lechler, P.J., Hudson-Edwards, K.A., Macklin, M.G., 2002. Lead isotopic fingerprinting of heavy metal contamination, Rio Pilcomayo basin, Bolivia. Geochemistry: Exploration, Environment, Analysis 2, 225-233.
Miller, J.R., Lechler, P.J., Mackin, M.G., Germanoski, D., Villarroel, L.F., 2007. Evaluation of particle dispersal from mining and milling operations using lead isotopic fingerprinting techniques, Rio Pilcomayo Basin, Bolivia. Science of the Total Environment 384, 355-373.
MonTec, 2007. Environmental assessment and remedial action plan (EARAP): Stan Trig/Stari Trg and Artana/Novo Brdo Mines, Kosovo. Available from: http://www.kosovo.undp.org/repository/docs/environment%20report.pdf,. Accessed: 10/11/13.
Morton, J., Carolan, V.A., Gardiner, P.H.E., 2002. Removal of exogenously bound elements from human hair by various washing procedures and determination by inductively coupled plasma mass spectrometry. Analytica Chimica Acta 455, 23-34.

Moya, J., Bearer, C.F., Etzel, R.A., 2004. Children's behavior and physiology and how it affects exposure to environmental contaminants. Pediatrics 113, 996-1006.
Nannoni, F., Protano, G., Riccobono, F., 2011. Uptake and bioaccumulation of heavy elements by two earthworm species from a smelter contaminated area in northern Kosovo. Soil Biology & Biochemistry 43, 2359-2367.
Okorie, A., Entwistle, J., Dean, J.R., 2012. Estimation of daily intake of potentially toxic elements from urban street dust and the role of oral bioaccessibility testing. Chemosphere 86, 460-467.
Palairet, M., 2003. Trepča, 1965-2000. United Nations Interim Mission in Kosovo, Pristina, p. 98.
Peck, P., 2004. Reducing Environment & Security Risks from Mining in South Eastern Europe. UNEP (ROE), Geneva, p. 186.
Pelfrene, A., Waterlot, C., Mazzuca, M., Nisse, C., Cuny, D., Richard, A., Denys, S., Heyman, C., Roussel, H., Bidar, G., Douay, F., 2012. Bioaccessibility of trace elements as affected by soil parameters in smelter-contaminated agricultural soils: A statistical modeling approach. Environmental Pollution 160, 130-138.
Pirkle, J.L., Kaufmann, R.B., Brody, D.J., Hickman, T., Gunter, E., Paschal, D.C., 1998. Exposure of the US population to lead, 1991-1994. Environmental Health Perspectives 106, 745-750.
Prathumratana, L., Kim, R., Kim, K.W., 2008. Heavy metal contamination of the mining and smelting district in Mitrovica, Kosovo, Proceedings of the International Symposia on Geoscience Resources and Environments of Asian Terranes, Bangkok, Thailand, pp. 479-482.
Riccobono, F., Baroni, F., Borgna, L., Di Lella, L.A., Nannoni, F., Pisani, A., Pizzetti, E., Protano, G., Rossi, S., 2004. Environmental Geochemistry of Soils of the Kosovska Mitrovica region (Northern Kosovo). University of Siena, Siena, p. 106.
Rodrigues, J.L., Batista, B.L., Nunes, J.A., Passos, C.J.S., Barbosa Jr., F., 2008. Evaluation of the use of human hair for biomonitoring the deficiency of essential and exposure to toxic elements. Science of the Total Environment 405, 370-376.
Rodushkin, I., Axelsson, M.D., 2000. Application of double focusing sector field ICP-MS for multielement characterization of human hair and nails. Part II. A study of the inhabitants of northern Sweden. Science of the Total Environment 262, 21-36.
Runow, K.D., 2005a. Investigation of the heavy metal load in refugee camps with Mitrovica in Kosovo: results of the hair analyses. Institute for Functional Medicine, Wolfhagen, p. 5.
Runow, K.D., 2005b. Investigation of the heavy metal load in refugee camps with Mitrovica in Kosovo: results of the hair analyses. Institute for Functional Medicine, Wolfhagen, p. 5.
Sinclair, A.J., 1974. Selection of threshold values in geochemical data using probability graphs. Journal of Geochemical Exploration 3, 129-149.
Sonke, J.E., Sivry, Y., Viers, J., Freydier, R., Dejonghe, L., Andre, L., Aggarwal, J.K., Fontan, F., Dupre, B., 2008. Historical variations in the isotopic composition of atmospheric zinc deposition from a zinc smelter. Chemical Geology 252, 145-157.
Sostaric, S.B., Palinkas, L.A., Topa, D., Spangenberg, J.E., Prochaska, W., 2011. Silver-base metal epithermal types of deposit Crnac, Rogozna Mts., Kosovo. Part 1: Ore mineral geochemistry and sulfur isotope study. Ore Geology Reviews 40, 65-80.
Soto-Jimenez, M.F., Paez-Osuna, F., Scelfo, G., Hibdon, S., Franks, R., Aggarawl, J., Flegal, A.R., 2008. Lead pollution in subtropical ecosystems on the SE Gulf of California Coast: a study of concentrations and isotopic composition. Marine Environmental Research 66, 451-458.
Spalinger, S.M., von Braun, M.C., Petrosyan, V., von Lindern, I.H., 2007. Northern Idaho house dust and soil lead levels compared to the bunker hill superfund site. Environmental Monitoring and Assessment 130, 57-72.
Stafilov, T., Aliu, M., Sajn, R., 2010. Arsenic in surface soils affaected by mining and metallurgical processing in K. Mitrovica region, Kosovo. International Journal of Environmental Research and Public Health 7, 4050-4061.
Tordoff, G.M., Baker, A.J.M., Willis, A.J., 2000. Current approaches to the revegetation and reclamation of metalliferous mine wastes. Chemosphere 41, 219-228.
Torrente, M., Colomina, M.T., Domingo, J.L., 2005. Metal concentrations in hair and cognitive assessment in an adolescent population. Biological Trace Element Research 104, 215-221.

Turner, J.N., Brewer, P.A., Macklin, M.G., 2008. Fluvial-controlled metal and As mobilisation, dispersal and storage in the Río Guadiamar, SW Spain and its implications for longer-term contaminant fluxes to the Doñana wetlands. Science of the Total Environment 394, 144-161.
Varrica, D., Tamburo, E., Dongarra, G., Sposito, F., 2014. Trace elements in scalp hair of children chronically exposed to volcanic activity (Mt. Etna, Italy). Science of the Total Environment 470, 117-126.
Veron, A., Flament, P., Bertho, M.L., Alleman, L., Flegal, R., Hamelin, B., 1999. Isotopic evidence of pollutant lead sources in Northwestern France. Atmospheric Environment 33, 3377-3388.
VROM, 2000. Circular on target values and intervention values for soil remediation, DBO/1999226863. Netherlands Government Gazette 39, 1-11.
Walraven, N., van Gaans, P.F.M., van der Veer, G., van Os, B.J.H., Klaver, G.T., Vriend, S.P., Middelburg, J.J., Davies, G.R., 2013. Tracing diffuse anthropogenic Pb sources in rural soils by means of Pb isotope analysis. Applied Geochemistry 37, 242-257.
Wang, T., Fu, J., Wang, Y., Liao, C., Tao, Y., Jiang, G., 2009. Use of scalp hair as indicator of human exposure to heavy metals in an electronic waste recycling area. Environmental Pollution 157, 2445-2451.
Wasserman, G.A., Liu, X., Popovac, D., Factor-Litvak, P., Kline, J., Waternaux, C., LoIacono, N., Graziano, J.H., 2000. The Yugoslavia Prospective Lead Study: contributions of prenatal and postnatal lead exposure to early intelligence. Neurotoxicology and Teratology 22, 811-818.
Wasserman, G.A., Liu, X.H., Lolacono, N.J., FactorLitvak, P., Kline, J.K., Popovac, D., Morina, N., Musabegovic, A., Vrenezi, N., CapuniParacka, S., Lekic, V., PreteniRedjepi, E., Hadzialjevic, S., Slavkovich, V., Graziano, J.H., 1997. Lead exposure and intelligence in 7-year-old children: The Yugoslavia prospective study. Environmental Health Perspectives 105, 956-962.
Yu, L., Oldfield, F., 1989. A multivariate mixing model for identifying sediment source from magnetic measurements. Quaternary Research 32, 168-181.
Zaman, M.S., Zereen, F., 1998. Growth responses of radish plants to soil cadmium and lead contamination. Bulletin of Environmental Contamination and Toxicology 61, 44-50.
Zhang, Y.P., Wang, X.F., Chen, H., Yang, X., Chen, J.M., Allen, J.O., 2009. Source apportionment of lead-containing aerosol particles in Shanghai using single particle mass spectrometry. Chemosphere 74, 501-507.


N
Sitnica
Žitkovac
Stan Tërg
Mine
Trepca
Zharkov Potok
tailings pond
Zveçan
Pb smelter
Gornje Polje
waste dumps
Cesmin Lug
Osterode
Bosniak Mahalla
Roma
Mahalla
MITROVICA
Ibar
Disused chemical
factory, battery plant
and Zn electrolysis
waste dumps
Sitnica
0
4 km
SERBIA
Leposavic
SERBIA
Mitrovica
MONTENEGRO
Pristina
KOSOVO
ALBANIA
MACEDONIA
0
50 km
Figure 1

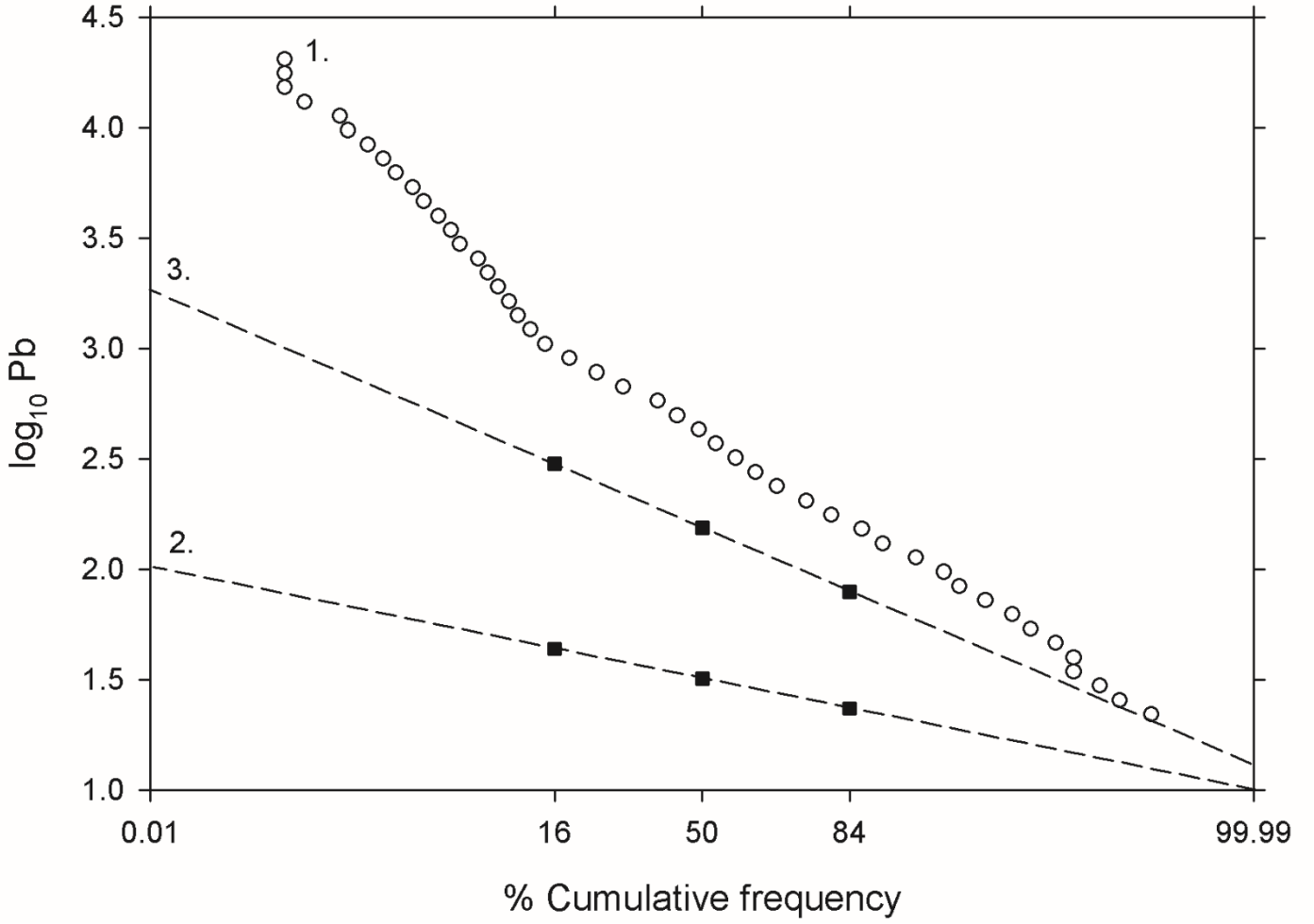

4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
log10 Pb
1.
2.
3.
0.01
16
50
84
99.99
% Cumulative frequency

Figure 2

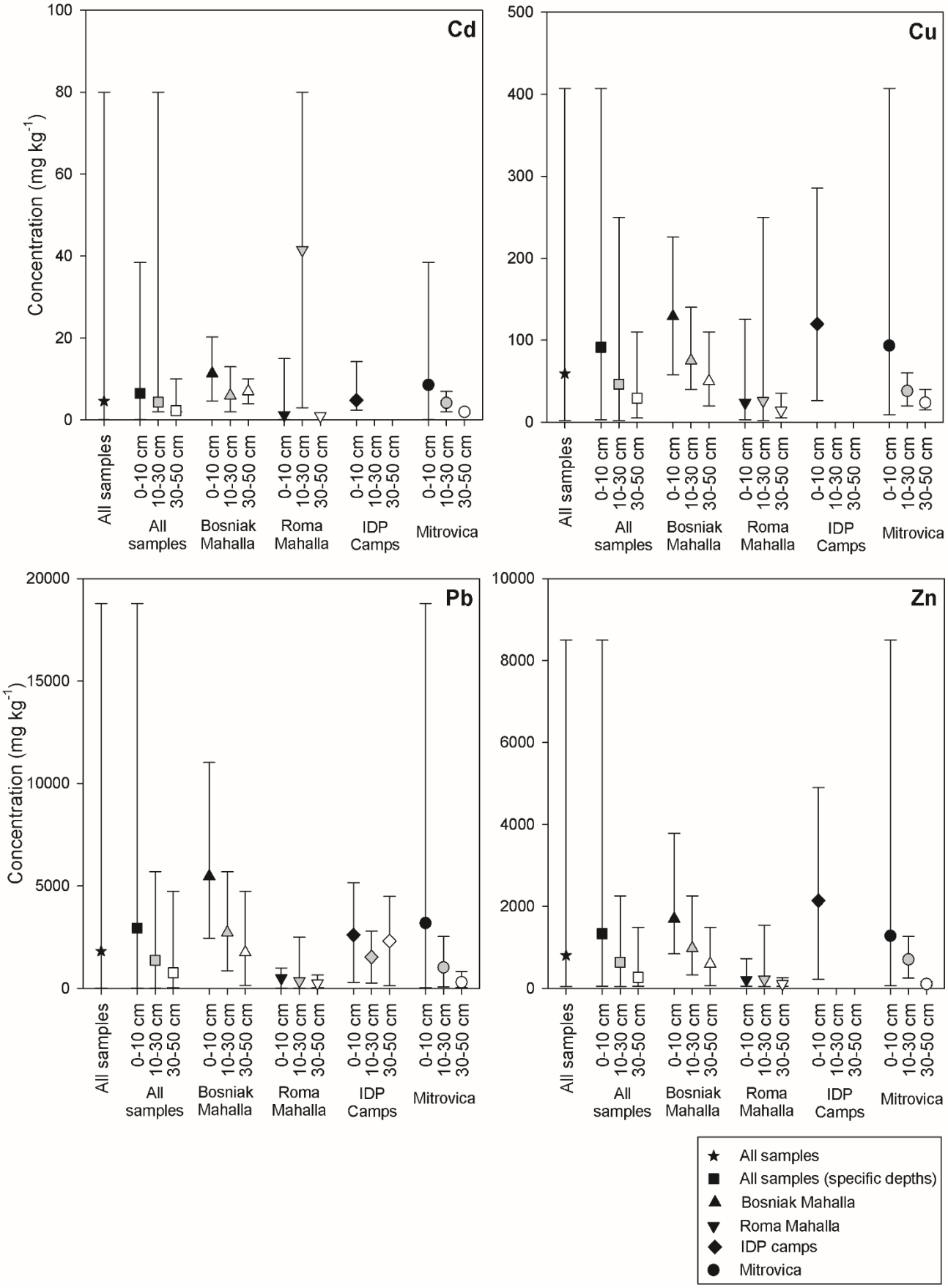

Cd
Cu
Pb
Zn
Concentration (mg kg-1)
All samples
0-10 cm
10-30 cm
30-50 cm
All samples
Bosniak Mahalla
Roma Mahalla
IDP Camps
Mitrovica
All samples
All samples (specific depths)
Bosniak Mahalla
Roma Mahalla
IDP camps
Mitrovica

Figure 3

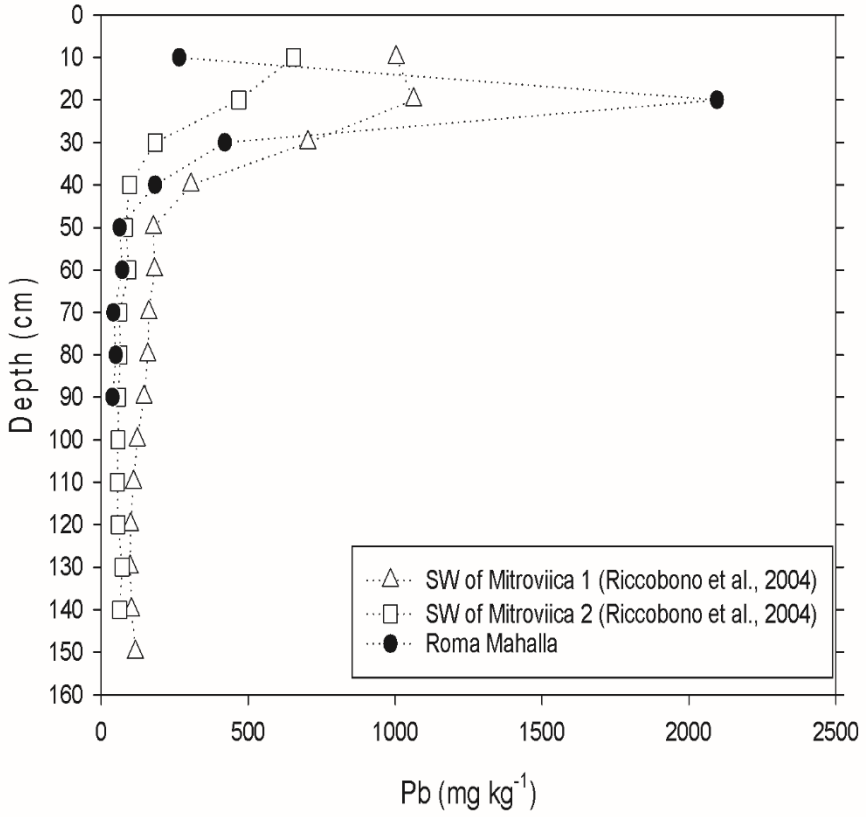

Depth (cm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
0
500
1000
1500
2000
2500
Pb (mg kg-1)
SW of Mitroviica 1 (Riccobono et al., 2004)
SW of Mitroviica 2 (Riccobono et al., 2004)
Roma Mahalla

Figure 4

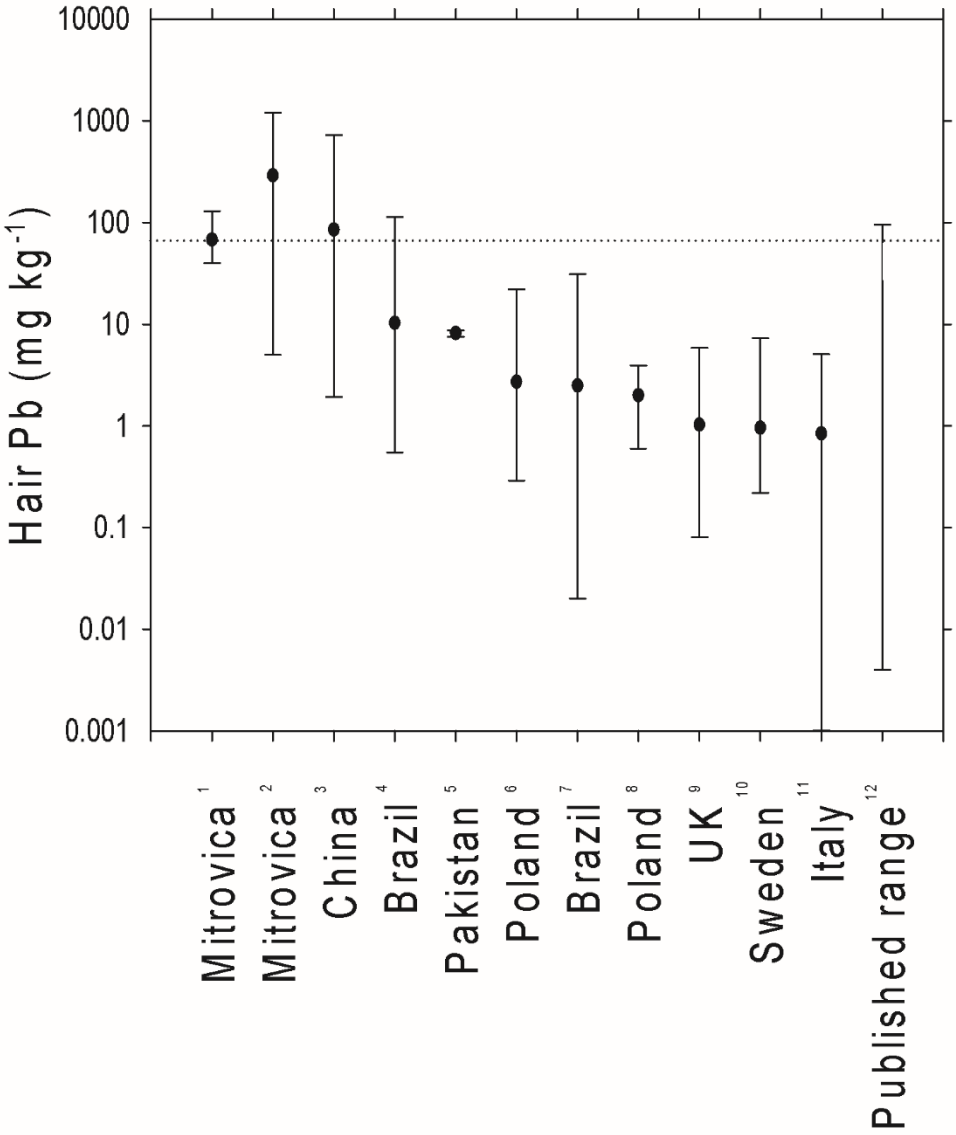

10000
1000
100
10
1
0.1
0.01
0.001
Hair Pb (mg kg-1)
Mitrovica 1
Mitrovica 2
China 3
Brazil 4
Pakistan 5
Poland 6
Brazil 7
Poland 8
UK 9
Sweden 10
Italy 11
Published range 12

Figure 5

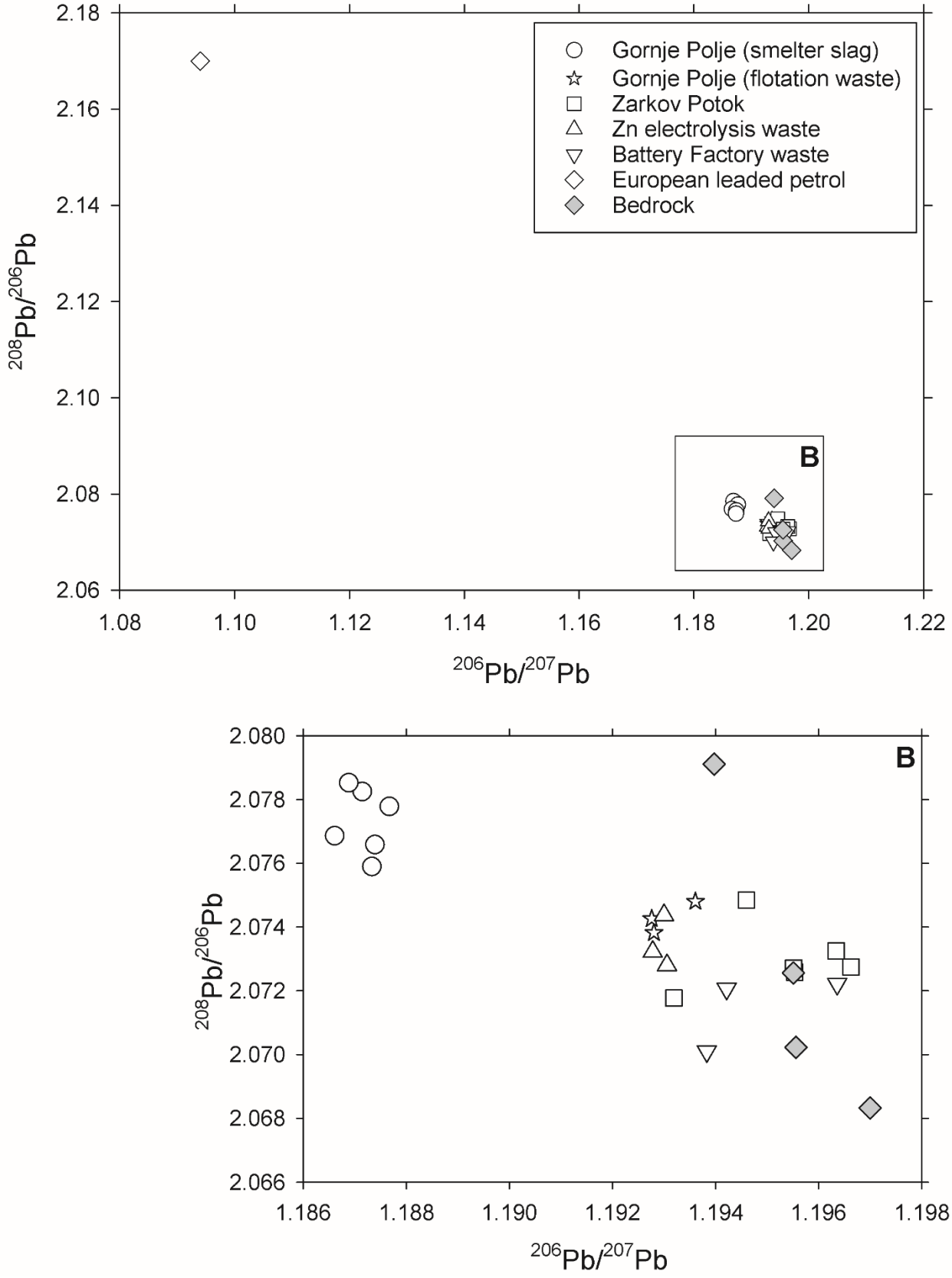

Gornje Polje (smelter slag)
Gornje Polje (flotation waste)
Zarkov Potok
Zn electrolysis waste
Battery Factory waste
European leaded petrol
Bedrock
B
$^{208}Pb/^{206}Pb$
$^{206}Pb/^{207}Pb$
2.18
2.16
2.14
2.12
2.10
2.08
2.06
1.08
1.10
1.12
1.14
1.16
1.18
1.20
1.22
2.080
2.078
2.076
2.074
2.072
2.070
2.068
2.066
1.186
1.188
1.190
1.192
1.194
1.196
1.198

Figure 6

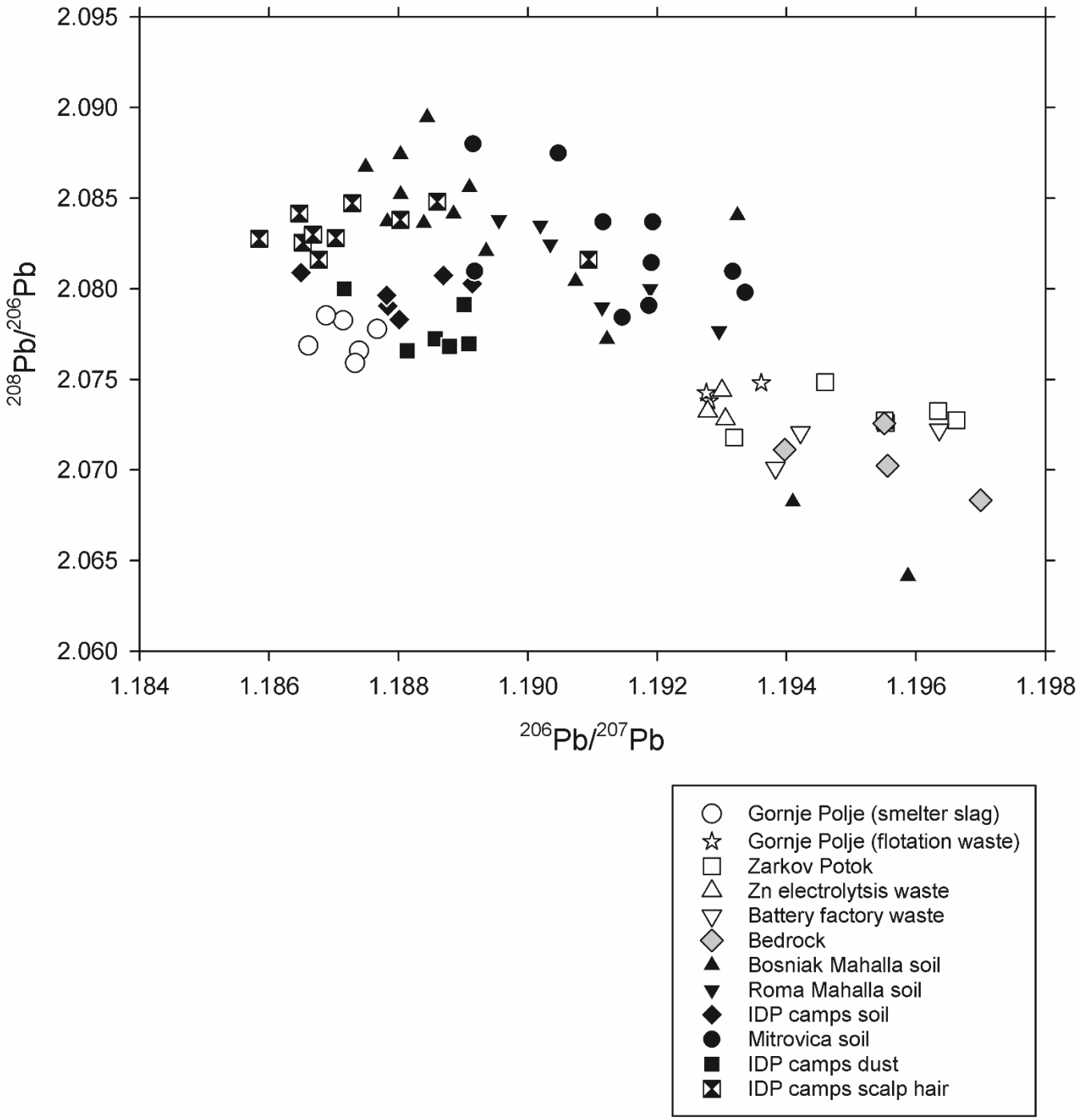

2.095
2.090
2.085
2.080
2.075
2.070
2.065
2.060
208Pb/206Pb
1.184
1.186
1.188
1.190
1.192
1.194
1.196
1.198
206Pb/207Pb
Gornje Polje (smelter slag)
Gornje Polje (flotation waste)
Zarkov Potok
Zn electrolytsis waste
Battery factory waste
Bedrock
Bosniak Mahalla soil
Roma Mahalla soil
IDP camps soil
Mitrovica soil
IDP camps dust
IDP camps scalp hair

Figure 7